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To cite this article: V K Karpasyuk *et al* 2019 *J. Phys.: Conf. Ser.* **1347** 012036

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Unusual properties and features of oxygen nonstoichiometry of La-Sr manganites with manganese replacement by a combination of nickel and germanium

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Abstract. When studying manganites of the system $\text{La}_{1-c}\text{Sr}_c\text{Mn}_{1-x}(\text{Ni}^{2+}_{0.5}\text{Ge}^{4+}_{0.5})_x\text{O}_{3+\gamma}$ ($x = 0.05; 0.10; 0.15; 0.15 \leq c \leq 0.35$), it was experimentally established that after reductive annealing, which leads the oxygen content to the stoichiometric one, unit cell volume (v) of the samples decreases and at $c \geq 0.19$ it is less than after annealing in oxygen. Based on the analysis of various charge compensation mechanisms using derived dependences of v on the oxygen content and taking into account the changes in magnetic and electrical parameters, it is established that experimental data can be explained only with the allowance for formation of singly charged oxygen ions. The relationships between magnetic parameters of the manganites and their composition, structural characteristics and deviations from oxygen stoichiometry are explained. The possibility of local ferromagnetic ordering of uncompensated spins of Ni^{2+} ions due to their interaction with singly charged O^- anions is considered.

1. Introduction

Among strongly correlated oxide systems, considerable attention is attracted to perovskite-like manganites, in which the effects of colossal magnetoresistance, giant magnetostriction, and electrical switching can be combined [1-4]. Manganites are phases of variable composition, they undergo a number of structural, magnetic and electronic transformations, characterized by the appearance of defects and inhomogeneities of various types, collective states, and self-organization processes [5-10]. Compositions in lanthanum-strontium system $\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3+\gamma}$ with $x < 0.5$ possess p -type conductivity, and when $x \geq 0.175$ at sufficiently low temperatures metal-like state takes place and coexists with ferromagnetism [1,6,7]. However, the concepts of holes concentration, their localization and transfer remain controversial.

Fundamental problems of the correlation between different types of ordering, Jahn-Teller effect and competitive interactions responsible for the magnetic and transport properties of manganites are closely



related to the mechanisms of charge compensation of the impurities and the deviation of oxygen from stoichiometric concentration [5,7,11-15].

Introduction of divalent or quadrivalent ions into manganites causes the doping of hole- or electron-type, correspondingly. At the same time, as emphasized in [1], the number of charge carriers in manganites, in general, is not equal to the number of introduced non-isovalent ions, since an impurity atom is electroactive only if it is isolated from other impurity atoms.

Along with the most often assumed mechanism of compensation of a divalent impurity or an increased oxygen concentration, realized by the $\text{Mn}^{3+} \rightarrow \text{Mn}^{4+}$ transition [7,12,15-17], there is the possibility of compensation due to the formation of singly charged oxygen ions (O^-) having an unpaired electron [5, 18]. In this case, the state of the holes can be of the oxygen type, and they can be antiferromagnetically bound to the high-spin configuration of the Mn^{3+} ion [1,19]. Then excitation of "electron-hole" pair means the transition of delocalized electron from the p -level of oxygen to the d -level of manganese, which are highly hybridized [20], and the conductivity occurs through the anion sublattice [7,22]. It should be noted that the existence of singly charged oxygen ions is also considered in related copper-oxide HTSC materials [21], strontium ferrite [22], and also in ferrogarnets [23].

X-ray photoelectron spectra of La-Sr manganites indicate [24] that in the region of manganese's formal valence from 3.0+ to 3.3+ holes have an $\text{O}2p$ character, and at higher valence holes are formed in $\text{Mn}3d$ states.

In [18] the data on the existence of singly charged oxygen ions in Ti-substituted La-Sr manganites with strontium content of more than 0.375 f.e. were obtained. With increasing titanium concentration the number of O^- increases. The metal-semiconductor transition temperature (T_{ms}) becomes much higher, which can be due to hybridization of d -levels of manganese and p -levels of titanium, as occurs in the interaction of manganese with oxygen [20].

An alternative to the formation of singly charged oxygen ions is the mechanism of divalent impurity compensation by anion vacancies, which can arise independently as a result of heat treatment in a reductive atmosphere [5,11,13,14]. At the same time, in appropriate number of cells the octahedral coordination of manganese ions is violated, and the indirect exchange interaction of $\text{Mn}^{3+}-\text{O}^{2-}-\text{Mn}^{3+}$ becomes negative. In general, it can be concluded that vacancies in anion sublattice considerably deteriorate the electromagnetic characteristics of manganites [11,13,14]; for example, the metal-like ferromagnetic behavior of a number of systems is realized only in the absence of oxygen vacancies [11,14].

With an increased oxygen content in the manganites, cation vacancies arise, which a priori can be located both in the octahedral sublattice (B) filled with manganese and other metal ions, and in the sublattice with a 12-fold oxygen environment (A), in which lanthanum and substitutional large ions, including strontium, are located. According to the works [12,15], vacancies are uniformly distributed in both sublattices, and in [5] it is assumed that they are localized mainly in the lanthanum-strontium sublattice.

Data concerning the effect of divalent (Mg^{2+} , Zn^{2+} , Ni^{2+}) and tetravalent (Ti^{4+} , Ge^{4+}) ions on phase composition and electromagnetic properties of the La-Sr manganite systems are given in [16,17], and the combined replacement of manganese by Ni^{2+} and Ti^{4+} ions, which are respectively acceptors and donors, was studied in [11], where the stability of manganite properties for annealing in atmospheres with different partial oxygen pressures was found.

In this paper we present the results of the investigation of $\text{La}_{1-c}\text{Sr}_c\text{Mn}_{1-x}(\text{Ni}^{2+}_{0.5}\text{Ge}^{4+}_{0.5})_x\text{O}_{3+\gamma}$ ($x = 0.05; 0.10; 0.15; 0.15 \leq c \leq 0.35$) manganites, which can only be explained by taking into account the formation of singly charged ions of oxygen after reductive annealing.

2. Experimental

Manganites were synthesized by ceramic processing. The initial components were dried powders La_2O_3 , SrCO_3 , MnO_2 , NiO , GeO_2 , procedures and conditions of the samples preparation for sintering are described in [16]. Sintering was carried out in air at 1473 K, the time of isothermal aging was 10 hours. Cooling of the samples occurred with the furnace.

A part of the sintered samples was annealed in vacuum at partial oxygen pressure in the gas phase $P_{O_2} = 10^{-1}$ Pa and temperature $T = 1223$ K to reach the stoichiometric oxygen concentration [16,5]; the other part was annealed in an oxygen atmosphere ($P_{O_2} = 10^5$ Pa) at the same temperature to study the effect of excess oxygen on the properties of manganites. The annealing was carried out for 96 hours.

Measurement methods of magnetization, Curie point and dc electrical characteristics are given in the work [18].

3. Results and discussion

Figure 1 demonstrates the dependences of rhombohedral unit cell volume on the composition of initial (sintered) and annealed under different conditions manganites.

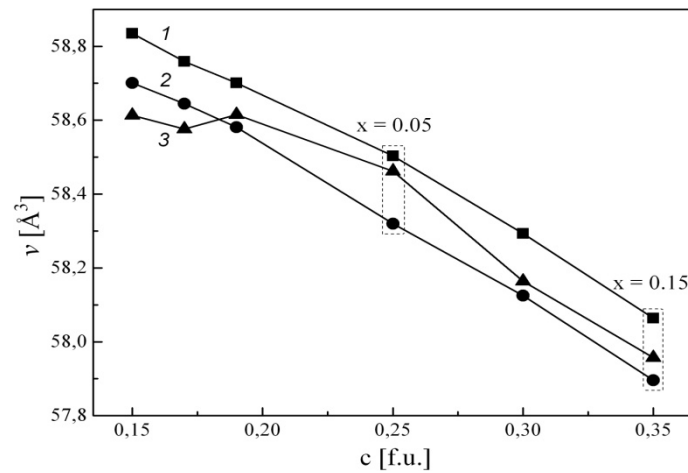


Figure 1. Unit cell volume v of manganites $La_{1-c}Sr_cMn_{1-x}(Ni^{2+}_{0.5}Ge^{4+}_{0.5})_xO_{3+\gamma}$ for different strontium contents at $x = 0.10$, and also at $x = 0.05, 0.15$ (shown in the figure): 1 – initial samples; 2 – after annealing in vacuum; 3 – after annealing in oxygen.

The decrease in the unit cell volume with increasing strontium concentration in manganites is an easily explainable effect for any mechanism of charge compensation of Sr^{2+} ions (the $Mn^{3+} \rightarrow Mn^{4+}$ transition, the formation of singly charged O^- or oxygen vacancies), taking into account the contribution of the corresponding ionic radii. The same applies to the influence of manganese substituents.

It is much more difficult to explain variations in v as a result of annealing which changes the oxygen content. In the initial samples nonstoichiometry index $\gamma > 0$, because, according to [5,16,17], manganites of the lanthanum-strontium system synthesized in air at temperatures in the 1173-1473 K range, are characterized by an excessive oxygen content. After annealing in oxygen, its concentration in manganites naturally increased. In samples annealed in vacuum at selected T , P_{O_2} , the oxygen content should be close to the stoichiometric value ($\gamma = 0$). Unit cell volume of these manganites at values of $c \geq 0.19$ is less than that of samples annealed in oxygen (figure 1). This fact indicates that the charge compensation mechanisms in the cases under consideration are different.

Let us consider the structural formulas of manganites with super-stoichiometric oxygen content ($\gamma > 0$) for various charge compensation versions.

For the mechanism $Mn^{3+} \rightarrow Mn^{4+}$ and the concomitant formation of vacancies in both cation sublattices, the structural formula for $\gamma < 1$ can be written as: $\{La^{3+}_{(1-c)(1-\gamma/3)}Sr^{2+}_{c(1-\gamma/3)}\square_{\gamma/3}\}[Mn^{3+}_{(1-x-c-2\gamma)(1-\gamma/3)}Mn^{4+}_{(c+2\gamma)(1-\gamma/3)}Me^{3+}_{x(1-\gamma/3)}\square_{\gamma/3}]O_3^{2-}$, where the symbol \square denotes cation vacancy, and $Me^{3+} = (Ni^{2+}_{0.5}Ge^{4+}_{0.5})$, since the introduction of two- and four-valent ions at equal concentrations is equivalent, from the viewpoint of charge compensation, to the replacement of manganese by trivalent ions. Let us calculate the change in the unit cell volume (Δv) after reductive

annealing, which brings the oxygen content to the stoichiometric, using Poix's method, modernized by Kesler [25, 26], according to algorithm given earlier [18]. We use the following effective values of the characteristic distances of the cation-anion in the octahedral sublattice [18]: $\beta_{\text{Mn}^{3+}} = 1.99 \text{ \AA}$, $\beta_{\text{Mn}^{4+}} = 1.83 \text{ \AA}$, $\beta_{\text{Ge}^{4+}} = 1.84 \text{ \AA}$, $\beta_{\square\square} = 2.248 \text{ \AA}$; $\beta_{\text{Ni}^{2+}} = 1.84 \text{ \AA}$ [27]; for ions with a coordination number of 12: $\theta_{\text{La}} = 2.72 \text{ \AA}$; $\theta_{\text{Sr}} = 2.80 \text{ \AA}$; $\theta_{\square} = 2.52 \text{ \AA}$. The increment of the unit cell volume when the index of non-stoichiometry is changed by $\Delta\gamma$ in the first approximation is described by the formula: $\Delta\nu(\text{\AA}^3) \approx 3\nu^{2/3}(-0.249 + 0.022c + 0.012x)\Delta\gamma$.

Under reduction $\Delta\gamma < 0$, and since $c \leq 0.35$, $x \leq 0.15$, then theoretically there should be $\Delta\nu > 0$, whereas according to experimental data the volume after vacuum annealing decreased.

If we assume that cation vacancies arise only in the lanthanum-strontium sublattice [5], then the volume increment will be: $(\Delta\nu)_{\square\text{A}}(\text{\AA}^3) \approx 3\nu^{2/3}(-0.174 + 0.022c + 0.012x)\Delta\gamma$.

In this case, the cell volume should theoretically also increase during reduction.

With oxidative firing, the value of γ increases, and the cell volume, respectively, becomes smaller. An additional contribution to the decrease of ν , besides an increase in the concentration of Mn^{4+} ions and cationic vacancies, in this case could be the formation of trivalent nickel ions [11], which in manganites are in low-spin state of Ni^{III} [28] and have a small ionic radius (0.56 \AA [27]).

Mechanism of the formation of vacancies in the anion sublattice would be effective from the viewpoint of reducing the unit cell volume during reductive annealing, but this mechanism seems unrealistic under our conditions because of the presence of super-stoichiometric oxygen in the initial samples (especially since nickel and germanium increase its content [16, 17]). In addition, the appearance of oxygen vacancies, according to [11,13,14], would lead to a sharp decrease in magnetic parameters and transition "metal-semiconductor" point T_{ms} , which in fact did not occur (table 1, figure 2). Magnetization and Curie temperature have changed very little, and T_{ms} has even increased in the last three samples (for example, in the sample $\text{La}_{0.65}\text{Sr}_{0.35}\text{Mn}_{0.85}(\text{Ni}_{0.5}\text{Ge}_{0.5})_{0.15}\text{O}_{3+\gamma}$ from 181 K to 188 K, figure 2), although resistance has increased.

Table 1. Magnetization in the field of 5.6 kOe at 80 K and Curie temperature of the initial and annealed samples of $\text{La}_{1-c}\text{Sr}_c\text{Mn}_{1-x}(\text{Ni}^{2+}_{0.5}\text{Ge}^{4+}_{0.5})_x\text{O}_{3+\gamma}$: I – initial; II – annealed in vacuum

Chemical formulae		σ , emu/g		T_c , K	
c	x	I	II	I	II
0.15	0.10	73.3	73.4	248	244
0.17	0.10	75.1	74.7	235	231
0.19	0.10	75.7	76.2	249	247
0.25	0.05	83.9	85.1	192	189
0.30	0.10	79.8	79.8	209	209
0.35	0.15	74.2	71.8	263	262

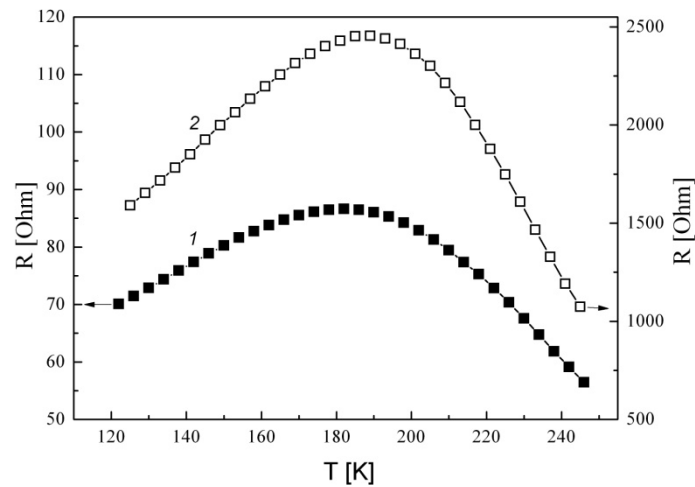


Figure 2. Temperature dependences of the resistance of manganites $\text{La}_{0.65}\text{Sr}_{0.35}\text{Mn}_{0.85}(\text{Ni}_{0.5}\text{Ge}_{0.5})_{0.15}\text{O}_{3+\gamma}$: 1 – initial sample; 2 – annealed in vacuum.

Let us consider the charge compensation mechanism associated with the formation of singly charged oxygen ions. In this case, the structural formula of the manganite will have the form: $\{\text{La}_{1-c}^{3+}\text{Sr}_c^{2+}\}[\text{Mn}_{1-c-x+\varepsilon}^{3+}\text{Mn}_{c-\varepsilon}^{4+}(\text{Ni}_{0.5}^{2+}\text{Ge}_{0.5}^{4+})_x]\text{O}_{3-\varepsilon}^{2-}\text{O}_\varepsilon^-$.

Since the ionic radius of O^- can be taken to be 1.1 Å [23], which is 0.26 Å smaller than the radius of the O^{2-} anion [27], the characteristic distances "cation- O^- " differ by the same amount from the above-mentioned "cation- O^{2-} " distances.

Taking into account that the fraction of cation bonds with singly charged anions is $\varepsilon/3$, and with doubly charged anions it is $(1-\varepsilon/3)$, we find that the change in the unit cell volume upon the occurrence of O^- ions will be: $\Delta v_\varepsilon (\text{\AA}^3) \approx -0.036\varepsilon v^{2/3}$. Thus, the formation of singly-charged oxygen ions (or, in other words, oxygen-type holes [1,21]) during reductive annealing should lead to a decrease in the unit cell volume, which corresponds to the experimental data. From these data one can calculate the concentration of singly charged anions. Estimated values of ε are in the range of 0.21-0.25 f.u. at $0.15 \leq c \leq 0.19$ and in 0.31-0.34 range at $0.25 \leq c \leq 0.35$.

It is interesting to note that the values of Δv exhibit a clear anticorrelation with $\Delta\sigma$ and a fairly significant correlation with ΔT_c (figure 3).

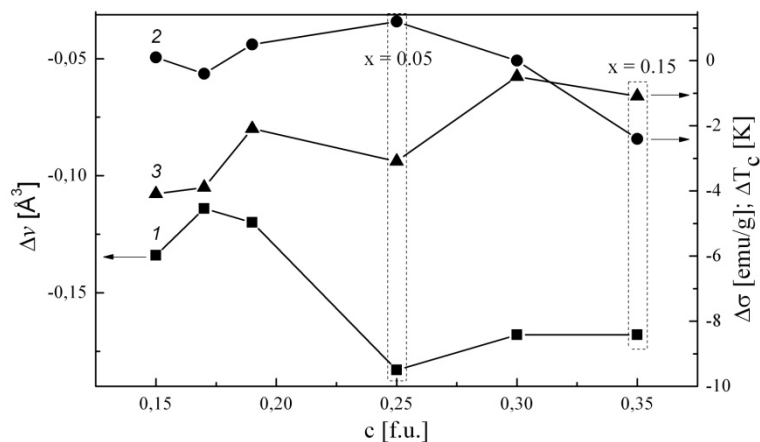


Figure 3. Changes in the parameters of manganites after annealing in vacuum: 1 – Δv ; 2 – $\Delta\sigma$; 3 – ΔT_c .

One of the factors that affect such behavior of the electromagnetic parameters of manganites can be the occurrence of a ferromagnetic bond between $\text{Ni}^{2+}(3d^8)$ ions through the O^- anion, especially since the latter, due to Coulomb forces, should be localized near divalent nickel ions, and nickel is prone to the formation of covalent bonds in oxides. A similar effect takes place, for example, in lanthanum cuprate doped with strontium, where the uncompensated spins of $\text{Cu}^{2+}(3d^9)$ ions align parallel to the spin of a singly charged oxygen ion [21]. On the other hand, Ni^{2+} ions shield Mn^{4+} , preventing double exchange interaction, and Ge^{4+} (by the way, geometrically and electrically indistinguishable from quadrivalent manganese) dilutes the sublattice of Jahn-Teller Mn^{3+} ions. These factors, taking into account also the interionic distances, explain the nonmonotonic changes in the parameters of manganites depending on the composition.

4. Conclusion

Thus, the paper gives an interpretation of revealed unusual behavior of the unit cell volume of manganites with paired substitution of divalent and quadrivalent ions for manganese during the reductive annealing, which leads the oxygen content to the stoichiometric one.

On the basis of the analysis of various mechanisms of charge compensation using the derived dependences of the unit cell volume on the oxygen content in manganites, it was found that the experimental data obtained can only be explained by taking into account the formation of singly charged oxygen ions. Connection of magnetic parameters of the manganites investigated with their composition, structural characteristics and deviations from stoichiometry is established and explained. In particular, attention is drawn to the possibility of the occurrence of local ferromagnetic ordering of uncompensated spins of Ni^{2+} ions due to the interaction of their electron shells with unpaired electron of singly charged O^- anions.

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